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Progress Report

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Studies of Elementary Reactions of Chemical Importance in the Atmospheres of Planets

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Progress Report
Fred L. Nesbitt
$CH_3 + CH_3$ Kinetics.

The recent detection of the methyl radical in the atmospheres of Saturn and Neptune prompted our measurement of the rate constant k_1 for

$CH_3 + CH_3 \rightarrow C_2H_6$

At low pressures and temperatures. We have completed our measurements of k_1 in the pressure range from 0.6 – 2 Torr at temperatures of 298 K, 202 K and 155 K and over a range of initial $[CH_3]$. These are the first measurements of k_1 at T = 155 K and the first low pressure data at 202 K. The experiments at 155 K required the construction of a new flow tube with a cooling jacket to the downstream end of the flow tube. The rate constant measurements for k1 in units of cm3 molecul-1 s-1 are: for T=298 K, k_1 = 2.15 at 0.6 Torr and 2.44 at 1.0 Torr; for T=202 K, k_1=5.04 at 0.6 Torr, 5.25 at 1.0 Torr and 6.52 at 2.0 Torr; for T=155 K, k_1=6.82 at 0.6 Torr, 6.98 at 1.0 Torr and 6.91 at 1.5 Torr.

Publication: Rate constant for the recombination reaction $CH_3 + CH_3 \rightarrow C_2H_6$ at T = 298K and 202 K, R.J. Cody, W.A. Payne, R.P. Thorn, F.L. Nesbitt, M.A. Iannone, D.C. Tardy and L.J. Stief, J. Phys. Chem., 106, 6050, 2002.

Fred L. Nesbitt and James Parker
Cl + CH_3 Kinetics.

The first direct measurements of the rate constant for the reaction $Cl + CH_3 \rightarrow CH_3Cl$ have been made. The rate constant has been measured at pressures between 0.5 and 2.0 Torr He and at temperatures of 298, 250 and 202 K. At T=202 K and P=1.0 Torr He, $k(Cl+CH_3)$=1.5x10-11 cm3molecule-1 s-1. As expected for a three body reaction, we observe $k(Cl+CH_3)$ to increase with pressure at all three temperatures. At any one

pressure, increases in k(Cl+CH_3) are observed as the temperature decreases. Theoretical studies are still in progress.

Progress Report
Benjamin P. Michael

Vibrational-to-translation (V-T) transfer rates for light hydrocarbons at low temperatures are important parameters in thermal-structure models of the upper atmospheres of the outer planets and their satellites. However, the required data are either simply not available or do not extend to the low temperatures found in those systems. Because methane is such an important constituent in outer planet atmospheres, we have initiated a program to measure the temperature dependence of (V-T) rates for its relaxation by appropriate collision partners. These rates are in turn used for the engineering development of, planning of, and the interpretation of data from a variety of planetary missions: Cassini/Huygens, Galileo Orbiter/Probe and Pluto-Kuiper Express.

Methane self-relaxation (V-T) rates from 300 to 90 K in approximately 10 K increments have been determined using a photoacoustic technique. This data represents the first ever-direct experimental results over this temperature range and extends the lowest temperature data point by over 60 K. The results from this data reveal that theoretical methods such as Landau-Teller and Schwartz. Slawsky and Herzfeld (SSH) can have significant deviations, especially at lower temperatures. A manuscript describing the experimental setup, operation and results is currently being completed.

An assessment of theoretical predictions, both Landau-Teller and Schwartz, Slawsky, and Herzfeld (SSH), for the relaxation (V-T) of methane by nitrogen was completed. The results were compared to the existing data for the interaction of methane with several monoatomic collision partners (helium, neon, and argon). A talk entitled "Assessment of

Model Predictions for the Relaxation of Methane by Nitrogen" was presented at the 33rd Annual Meeting of the American Astronomical Society (AAS) Division of Planetary Sciences meeting in New Orleans, LA.

Direct measurements of the relaxation of methane by nitrogen have been completed from 300 to 200 K in 20 K increments. This data represents the first experimental results of the methane – nitrogen system at other then room temperature. Preliminary results show the relaxation rate to be approximately 20% less then the expected values. This work will be presented at the 34th Annual Meeting of the American Astronomical Society in Birmingham, AL. Current work continues on determining the rates for the relaxation of methane by nitrogen as a function of temperature down to 90 K.

Progress Report
Frank T. Ferguson

There are many unanswered question as to the origin of cosmic dust grains, but it is generally believed that a significant fraction of these grains are refractory species such as silicates or graphite that condense in the outflows of stars. The exact conditions under which these refractory vapors condense are unknown and there is very little experimental data on the condensation of these species. Our research is focused on understanding how these materials nucleate to form solid particles and later grow and coagulate into larger bodies such as planetesimals. Listed below are various areas of our research related to filling this void in our knowledge.

Thermogravimetric Determination of Vapor Pressure

An accurate knowledge of equilibrium vapor pressure data is critical in applying nucleation theories. Unfortunately, these data are typically poorly known for high-temperature, refractory species. We have initiated a series of experiments to measure the

vapor pressure of such species using a thermogravimetric device. Very precise changes in sample weight due to evaporation are used to calculate the equilibrium vapor pressure. Our first series of runs gave erratic results, but we have just recently constructed an improved sample cell. Using this cell we have been able to achieve excellent agreement between our experimental measurements of copper vapor pressure and previous data. Now that we have verified that the apparatus is functioning correctly we are using this system to measure the vapor pressure of higher temperature species, (iron and silicon monoxide), which are of more astrophysical relevance.

Refractory Nucleation Data

In this work we are trying to measure the conditions (supersaturation and temperature) where metals nucleate. To achieve this we resistively heat materials within an inert gas and measure the conditions at the interface between vapor and condensed smoke particles (onset of nucleation). We have completed a study of sodium nucleation and have just recently begun a study of potassium vapor. During our analysis of sodium vapor data we have determined that we will have to correct for vapor depletion effects and we are currently performing detailed modeling of this effect.

Thermal Diffusion Cloud Chamber

Approximately half of all the nucleation data presented in the literature has been taken using a device called the thermal diffusion cloud chamber. Only recently, researchers have noted that the experimental data seems to indicate an effect due to the background gas used in the chamber, even though such an effect is not predicted by current nucleation theories. We have recently submitted papers that show that much, (if not all), of this effect is due to hydrodynamic flow induced by buoyancy. This additional flow term is

not presently included in modeling of chamber conditions. We are continuing our work in trying to understand and account for this effect as well as trying to extend the available operating range of the current cloud chamber.

Publications

"A note on the phenomena of diffusive slip," Frank T. Ferguson, *Physics of Fluids*, 2002 submitted.

"The effect of carrier gas pressure and wall heating on the operation of the thermal diffusion cloud chamber," Frank T. Ferguson, Richard H. Heist, and Joseph A. Nuth, III, *Journal of Chemical Physics*, **115**, 10828, 2001.

"The impact of convective flow on thermal diffusion cloud chamber operation," Frank T. Ferguson and Richard H. heist, *Journal of Physical Chemistry-B*, **105**, 11828, 2001.

"Application of scaled nucleation theory to metallic vapor condensation," Daniel M Martinez, Frank T. Ferguson, Richard H. Heist, Joseph A. Nuth, III, *Journal of Chemical Physics*, **115**, 310, 2001.

Progress Report
Robert N. Nelson

Most of the work this year was focused on completion, calibration, and testing of "ACTS-II" the Absolutely Calibrated Tunable Sunphotometer - Two Channel. Both of the circular variable filters [CVF] used for wavelength selection were calibrated to give accurate values of wavelength vs. angle. Following assembly of the system, each channel was first calibrated for response (signal output vs. light input) using a blackbody source. The channels were then absolutely calibrated using several lasers

whose power was known. The completed system was set up at the Goddard Optical Site and two days of solar observation were carried out. This "first light" data will be used to decide what changes or improvements are needed. The other task was work up of vapor pressure data to obtain thermodynamic data on heat of vaporization and sublimation of ethylene and acetylene. This data was presented at the 2002 DPS meeting in Birmingham, AL, October 6-11, 2002.